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Gibbs free energy of hydrogen bonding of aliphatic alcohols with liquid water at 298 K

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ABSTRACT

Thermodynamics of hydrogen bonding between water and molecules of aliphatic alcohols in dilute aqueous solutions is studied. The Gibbs free energies of hydrogen bonding of normal aliphatic alcohols from methanol to octanol with liquid water are determined from experimental data. The molar fractions of free unbonded molecules of alcohols and monomeric species of water are reported. Strong cooperative effects are observed when an alcohol molecule binds to an associate of water, leading to huge negative values of the Gibbs energies and an increased aqueous solubility. Formation of the second and third hydrogen bonds of an alcohol molecule with water is much less favorable, what can be described as an anti-cooperative effect.

1. Introduction

Hydrogen bonds between the molecules of aliphatic alcohols and water have attracted a close attention of researchers for a long time. They have been studied using experimental (Raman and infrared [1], NMR [2], X-ray [3], neutron diffraction [4], calorimetry [5], dielectric relaxation [6]) and theoretical (quantum chemistry calculations [7], molecular dynamics [8], thermodynamic models [9]) methods in different phases and media (water–alcohol mixtures [10], apolar solvent [11], gas phase [12], solid matrices [13], molecular beams [14], crystals [15], solid–gas [16] and solid–liquid interfaces [17]) in order to determine their energetic, dynamical and structural properties.

Such interest is explained by both practical importance of alcohol–water systems and simple chemical nature of aliphatic alcohols which allows using them as a model for more complicated hydrogen-bonding molecules. Alcoholic hydroxyls are one of the most common and important functional groups in organic and biological chemistry. They are present in many bioactive molecules and in the active sites of biomacromolecules. Hydroxylic groups are often involved in noncovalent hydrogen bonding between biomolecules or between a biomolecule and aqueous medium. They can also be introduced to a newly synthesized hydrophobic molecule in order to increase its hydrophilicity.

An increase in the solubility of a molecule due to the introduction of functional groups is determined by the strength of hydrogen bonds that these groups form with water. The process of binding of substrates with receptors and enzymes is accompanied with dehydration of the groups that take part in binding. Thus, the constants of binding are also strongly influenced by the hydrogen bonding of alcoholic hydroxyls with water.

The strength of hydrogen bonding of water with a dissolved compound (A) or its single functional group can be characterized with the standard Gibbs energy of bonding $\Delta_{HB}G$, which is related to the fraction of free non-bonded molecules (groups) α, and to the effective constant of complexation with water K, through the following equation:

$$\Delta_{HB}G^{A/H_2O} = RT\ln\ \alpha^{A/H_2O} = -RT\ln(1+K) \quad (1)$$

This quantity ($\Delta_{HB}G^{A/H_2O}$) contributes to the Gibbs energy of hydration and to the Gibbs energy of dehydration or binding to another molecule in water with the opposite sign. Despite their importance, the Gibbs energies of H-bonding with liquid water at room temperature (298 K) for alcohols are still not reported. Their quantification is the goal of the present work.

2. Methodology

2.1. The problem of measuring thermodynamic functions of solute–solvent hydrogen bonding

The simplest systems to study the process of hydrogen bonding of alcohols with liquid water are their infinitely diluted aqueous

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